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On the contact conditions for the charge profile in the theory of the electrical double layer for nonsymmetrical electrolytes.

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The contact value of the charge profile for nonsymmetrical electrolytes is presented as the sum of three contributions. One of them is the normal component of the Maxwell electrostatic stress tensor. The second one is the surface electrostatic property defined as the integral of the product of the gradient of the electrical potential and the density distribution function of coions. The third term is the bulk contribution defined by the sum for anions and for cations of the product of their charge and their partial pressure. For noncharged surfaces only the last two are present and have the same sign in the case of size asymmetry. In the case of charge asymmetry the contact value of the charge profile is the result of the competitions of bulk and surface terms in which the bulk term is dominant. Using both the contact theorems for the density and the charge profiles, the exact expressions for the contact values of the profiles of coions and counterions are obtained and some related properties are discussed.

The properties of the electrical double layer are described by the density and charge profiles $\rho(z)$ and $q(z)$. They are connected with the density distribution functions $\rho_\alpha(z)$ for ions of type α having the charge e_α by the relations

$$\rho(z) = \sum_{\alpha} \rho_{\alpha}(z) \quad (1)$$

$$q(z) = \sum_{\alpha} e_{\alpha} \rho_{\alpha}(z) \quad (2)$$

where z is the normal distance from the wall.

For the contact value (CV) of the density and charge profiles, for the primitive model of electrolyte solutions, exact relations have established known as the contact theorems (CTs). The CT for the density profile states that the CV of the number density profile ρ^{ct} is given by the sum of the bulk electrolyte pressure P and the electrostatic Maxwell stress tensor contribution [1, 2]

$$\rho^{ct} \equiv \rho(d/2) = \beta P + \beta \frac{\varepsilon E^2}{8\pi} \quad (3)$$

where d is the ion diameter, assumed to be the same for all species, $\beta = 1/(k_B T)$ with k_B the Boltzmann constant and T the absolute temperature, ε is the dielectric constant of the solvent, $\varepsilon E/4\pi = q_s$ is the surface charge density per unit area on the wall. The CT for the charge profile was formulated recently by Holovko et al. [3]. In contrast to the theorem for the density profile, the CV of the charge profile q^{ct} has a nonlocal character and in general can be presented in the form

$$q^{ct} \equiv q(d/2) = \beta \int_{d/2}^{\infty} \hat{\rho}(z) \frac{\partial \psi(z)}{\partial z} dz + \beta \sum_{\alpha} e_{\alpha} P_{\alpha} \quad (4)$$

where $\hat{\rho}(z) = \sum_{\alpha} e_{\alpha}^2 \rho_{\alpha}(z)$, $\psi(z)$ is the electrical potential

$$\psi(z) = -\frac{4\pi}{\varepsilon} \int_z^{\infty} q(z_1)(z_1 - z) dz_1 \quad (5)$$

and P_α is the bulk partial pressure for ions of type α .

Both CTs (3) and (4) can be obtained by direct integration of the system of Born-Green-Yvon (BGY) equations for the singlet distribution functions $\rho_\alpha(z)$ [3, 4]. This procedure can be easily repeated for an electrolyte with different ion diameters d_α and leads to changing only ρ^{ct} and q^{ct} in relations (3) and (4) by the corresponding CVs given by

$$\rho^{ct} = \sum_{\alpha} \rho_{\alpha}(d_{\alpha}/2) \quad (6)$$

$$q^{ct} = \sum_{\alpha} e_{\alpha} \rho_{\alpha}(d_{\alpha}/2) \quad (7)$$

and the bulk partial pressure P_α according to the virial expression for the bulk pressure of a ion hard sphere system [5] is given by

$$\beta P_\alpha = \rho_\alpha \left(1 + \frac{2}{3} \pi \sum_{\gamma} \rho_\gamma d_{\alpha\gamma}^3 g_{\alpha\gamma}(d_{\alpha\gamma}^+) \right) + \frac{1}{3} \beta E_\alpha^{Coul} \quad (8)$$

where $d_{\alpha\gamma} = (d_\alpha + d_\gamma)/2$, $g_{\alpha\gamma}(d_{\alpha\gamma}^+)$ is the CV of the pair distribution function $g_{\alpha\gamma}(r)$ and

$$E_\alpha^{Coul} = \frac{1}{2} \rho_\alpha \sum_{\gamma} 4\pi \rho_\gamma \frac{e_\alpha e_\gamma}{\varepsilon} \int_0^\infty g_{\alpha\gamma}(r) r dr \quad (9)$$

is the coulombic part of the partial internal energy.

For the symmetrical electrolyte $\hat{\rho}(z) = e^2 \rho(z)$ (e being the elementary charge), it was shown [6] that the CV of the charge profile can be presented as the sum of the normal component of the Maxwell electrostatic stress tensor and a new electrostatic property defined by the integral of the product of the gradient of the electrical potential and the singlet distribution function of coions (ions having the identical sign as the surface charge). In this note we generalize this result for nonsymmetrical electrolytes and discuss some specific properties connected with the charge and size asymmetry of cations and anions.

First, we consider a nonsymmetrical electrolyte with a single type of anion and of cation, ρ_\pm , e_\pm and d_\pm are respectively the densities, charges and diameters of the ions and $\hat{\rho}(z)$ can be written as

$$\hat{\rho}(z) = e_+^2 \rho_+(z) + e_-^2 \rho_-(z) \quad (10)$$

$$= e_\mp q(z) - e_\pm \rho_\pm(z) (e_\mp - e_\pm) \quad (11)$$

where the upper/lower sign are relative to a positively/negatively charged surface. As a result the CT for the charge profile for nonsymmetrical electrolyte can be presented in the following form

$$q^{ct} = \beta e_\mp \frac{\varepsilon E^2}{8\pi} - \beta e_\pm (e_\mp - e_\pm) \mathcal{J}_\pm + \beta (e_+ P_+ + e_- P_-) \quad (12)$$

where

$$\mathcal{J}_\pm = \int_{d_\pm/2}^\infty dz \frac{\partial \psi(z)}{\partial z} \rho_\pm(z) \quad (13)$$

$\rho_\pm(z)$ is the density distribution function for coions near a positively/negatively charged surface. The result obtained is the generalization of our previous result [6] for the CV of the charge profile of the symmetrical electrolyte to the nonsymmetrical case. Similar as for the symmetrical electrolyte expression (12) has a simple interpretation. The difference between forces from counterions and coions required to obtain q^{ct} is connected with three contributions: the electrostatic Maxwell stress tensor contribution, the electrostatic contribution from coions described by the electrostatic property \mathcal{J}_+ or \mathcal{J}_- depending on the sign of the surface charge and a special combination of the partial pressures for coions and counterions.

From the CTs for the density and charge profiles presented in their form (3) and (12), it is possible to obtain the following exact relations for the CVs of the density profiles for coions and counterions respectively

$$\begin{aligned} \rho_+^{ct} \equiv \rho_+(d_+/2) &= \beta P_+ + \beta e_+ \mathcal{J}_+, \\ \rho_-^{ct} \equiv \rho_-(d_-/2) &= \beta P_- + \beta \frac{\varepsilon E^2}{8\pi} - \beta e_+ \mathcal{J}_+ \end{aligned} \quad (14)$$

for a positively charged surface or

$$\begin{aligned}\rho_+^{ct} &\equiv \rho_+(d_+/2) = \beta P_+ + \beta \frac{\varepsilon E^2}{8\pi} - \beta e_- \mathcal{J}_-, \\ \rho_-^{ct} &\equiv \rho_-(d_-/2) = \beta P_- + \beta e_- \mathcal{J}_-\end{aligned}\quad (15)$$

for a negatively charged surface. Since the CV of the density profile of coions cannot be negative, we also have the following conditions

$$P_+ + e_+ \mathcal{J}_+ \geq 0 \quad (16)$$

for a positively charged surface or

$$P_- + e_- \mathcal{J}_- \geq 0 \quad (17)$$

for a negatively charged surface.

These inequalities reduce to equalities in the limit $E \rightarrow \infty$ and as a consequence we have an exact cancellation of $e_+ \mathcal{J}_+$ (or $e_- \mathcal{J}_-$) by the partial pressure P_+ (or P_-). Similar as for the symmetrical electrolyte in the limit of small E , \mathcal{J}_+ (or \mathcal{J}_-) has a linear dependence on E and we can conjecture that \mathcal{J}_+ (or \mathcal{J}_-) is a monotonic function of E .

However, for a noncharged surface ($E = 0$) and nonsymmetrical electrolytes, the charge profile $q(z)$ is not zero in contrast to the symmetrical case. The charge and/or size asymmetry of cations and anions induces a double layer with an associated surface potential [7, 8]. According to the CT eq. (12), the CV of the charge profile for a noncharged surface is defined by two terms

$$q^{ct} = -\beta e_+(e_- - e_+) \mathcal{J}_+ + \beta(e_+ P_+ + e_- P_-) \quad (18)$$

$$= -\beta e_-(e_+ - e_-) \mathcal{J}_- + \beta(e_+ P_+ + e_- P_-). \quad (19)$$

Both forms for the CV of the charge are equivalent and due to this for a noncharged surface we have the following symmetrical relation

$$e_+ \mathcal{J}_+ + e_- \mathcal{J}_- = 0. \quad (20)$$

We may now distinguish the electrical double layer due to the charge and size asymmetry of ions for they are different in nature.

The influence of size asymmetry has a short-ranged steric origin since the smallest ion can approach the surface more closely than the larger ions. If we consider for simplicity a charge symmetrical electrolyte ($e_+ = -e_- = e$) according to relation (18)

$$q^{ct} = 2\beta e^2 \mathcal{J}_+ + \beta e(P_+ - P_-). \quad (21)$$

Due to electroneutrality, the first layer constituted of the smaller ions has to be compensated by the following layer where we find the larger ions. Then intuitively, the CV of the profile for the larger ions which are further from the wall has to be larger in order to compensate the profile for the smaller ions which starts before as they can come closer to the wall. For example, for the case $d_+ < d_-$ we will have $\rho_+^{ct} < \rho_-^{ct}$ and q^{ct} will be negative. This intuitive result is indeed in agreement with the CT for the charge given in eq. (21). For this case $(d\psi(z)/dz) < 0$ and according to definition eq. (13) $\mathcal{J}_+ < 0$ thus the first term of eq. (21) is negative. The second term at least for small ion concentration is also negative since the dominant contribution to the partial pressure comes from the Coulombic part of the partial internal energy eq. (9) which is more negative for smaller ions. This means that in this case q^{ct} will be negative in agreement with the intuitive statement. For the opposite case $d_+ > d_-$, $\rho_+^{ct} > \rho_-^{ct}$ and q^{ct} will be positive. This result also corresponds to the CT (21) as in this case $(d\psi(z)/dz) > 0$, $\mathcal{J}_+ > 0$ and in parallel $P_+ > P_-$ and q^{ct} will be positive.

The influence of the charge asymmetry on q_{ct} is different. It is associated with the electrostatics and results from the long-range behaviour of the profiles of the cations and anions leading to an exclusion effect by the neutral surface [7, 8]. From [9], when the conditions are such that electrostatic interactions become important in comparison to steric effects, we know for symmetrical electrolytes that the density profile decreases when we approach the wall producing a negative adsorption of ions. This effect is more pronounced the higher the charge of the ions. Now this phenomenon can be generalized to ions with different charges where to simplify we consider size symmetrical electrolytes ($d_+ = d_- = d$). And as a consequence, the CV of the charge for the ion carrying the higher charge will be smaller resulting in a CV of the charge profile negative for highly charged cations and positive for highly

charged anions. For example in the case $e_+ > |e_-|$, $e_+\rho_+^{ct} < |e_-|\rho_-^{ct}$ and $q^{ct} \leq 0$. In this case $(d\psi(z)/dz) > 0$, $\mathcal{J}_+ > 0$ and the first term of eq. (18) is positive. The second term in expression (18) is negative since for highly charged ions the coulombic part of the partial internal energy is more negative than for weakly charged ions and thus $e_+P_+ + e_-P_- < 0$. However, this term must be sufficiently negative in order to partially cancel the first positive term in the expression of q^{ct} and obtain an overall negative value for q^{ct} . For the case $e_+ < |e_-|$, q^{ct} will be positive. In this case, $(d\psi(z)/dz) < 0$, $\mathcal{J}_+ < 0$ and the first term of q^{ct} is negative. The second term is positive and again it must cancel partially the first negative term in order to have $q^{ct} \geq 0$. We can see that the sign of q^{ct} for the charge asymmetrical case is the result of the partial compensation of the bulk term, which is the sum of the product of ionic charges with the partial pressure of ions, and the surface term connected with the electrostatic property \mathcal{J}_+ . Both contributions have opposite signs but the bulk contribution must be dominant.

The simultaneous consideration of charge and size asymmetry effects is more complex. Nevertheless, expressions (18-19) for the CV of the charge profile are correct for this case also. It is clear that in some situations these two effects can enhance each others' influence and in other situations they can weaken or even cancel each other.

In this paper, results previously obtained for symmetrical electrolytes [6] are generalized for charge and/or size asymmetric systems. It is shown that the CV of the charge profile can be presented as the sum of three contributions. One of them is the normal component of the electrostatic Maxwell stress tensor. The second one is the electrostatic contribution from coions, described by the electrostatic property \mathcal{J}_+ or \mathcal{J}_- depending on the sign of the surface. Similar as for the symmetrical case [6], \mathcal{J}_+ or \mathcal{J}_- are defined by the integral from the product of the gradient of the electrical potential and the density distribution function of coions near the charged surface. The third term is the bulk contribution defined by the sum of the product of the charges of the coions and counterions multiplied by their corresponding partial pressures. Using the CTs for the charge and density profiles, the exact expressions for the CVs of the density profiles for coions and counterions are presented and discussed. We have also discussed the influence of the charge and size asymmetry on the CV of the charge profile for a noncharged surface. For noncharged surfaces, from the CT for the charge, the CV of the charge profile now only has two contributions, the Maxwell tensor being zero. We show that in the case of size asymmetry both contributions have the same sign which corresponds to the sign of the CV of the charge profile. In the case of charge asymmetry the two contributions have opposite signs. However the bulk contribution is dominant and imposes its sign to the CV of the charge.

Finally, the generalization of the results we have obtained for the more than two components case faces the principal difficulty related with the problem of expressing $\hat{\rho}(z)$ using the charge profile $q(z)$ and the coion density functions as in eq. (11). This problem can be solved only for the electrolyte with a single type of counterions. In this case, for example, for the positively charged surface

$$\begin{aligned} q^{ct} &\equiv \sum_{\alpha} e_{+\alpha} \rho_{+\alpha}(d_{+\alpha}/2) + e_- \rho_-(d_-/2) \\ &= \beta e_- \frac{\varepsilon E^2}{8\pi} - \beta \sum_{\alpha} e_{+\alpha} (e_- - e_{+\alpha}) \mathcal{J}_{+\alpha} + \beta e_- P_- + \sum_{\alpha} e_{+\alpha} P_{+\alpha} \end{aligned} \quad (22)$$

where

$$\mathcal{J}_{+\alpha} = \int_{d_{+\alpha}/2}^{\infty} \rho_{+\alpha}(z) \frac{\partial \psi(z)}{\partial z} dz. \quad (23)$$

From eq. (3) and (22) we can obtain that

$$\sum_{\alpha} (e_- - e_{+\alpha}) \rho_{+\alpha}(d_{+\alpha}/2) = \beta \sum_{\alpha} (e_- - e_{+\alpha}) P_{+\alpha} + \beta \sum_{\alpha} (e_- - e_{+\alpha}) e_{+\alpha} \mathcal{J}_{+\alpha}. \quad (24)$$

However this equation is not sufficient to obtain the expressions for the CV of the ionic density profiles in a similar way as starting from expression (12).

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